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Carbamates: A Directing Group for Selective C−H Amidation and Alkylation under Cp*Co(III) Catalysis

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Cite This: https://dx.doi.org/10.1021/acs.orglett.0c00589 Read Online

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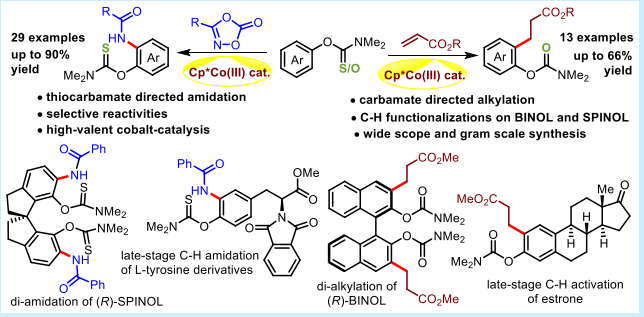
ABSTRACT: The selective reactivity of carbamate and thiocarbamate toward alkylation and amidation is reported under stable, high-valent, cost-effective cobalt(III) catalysis. This method reveals the wide possibility of designing a different branch of synthetically challenging yet highly promising asymmetric catalysts based on BINOL and SPINOL scaffolds. Late-stage C−H functionalization of L-tyrosine and estrone was also achieved through this approach. The mechanistic study shows that a base-assisted internal electrophilic substitution mechanism is operative here.



The ortho functionalization of aromatic phenols is the linchpin for the design and synthesis of numerous chiral ligands and catalysts.[1] In addition, 2-amino and alkylated phenols are key building blocks present in several biologically active heterocycles, drug molecules, and also important synthetic intermediates (Figure 1).[2] The known methods,

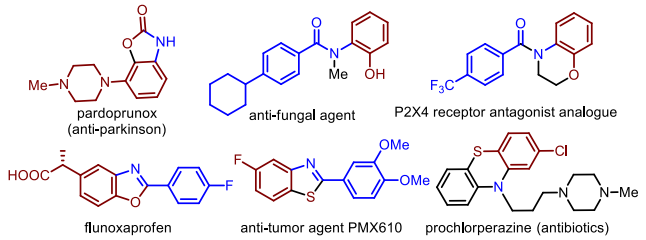


Figure 1. 2-Amido-phenol-derived bioactive molecules.

such as the Friedel−Crafts reaction, the Buchwald−Hartwig coupling, and ortho-lithiation strategies, suffer from a lack of regioselectivity, requiring prefunctionalized substrates, harsh reaction conditions, longer reaction sequences, and poor yields, restricting them from much broader applications.[3,4] This motivated us to develop new strategies based on regioselective 3,3′-functionalizations of indispensable BINOL, biphenyl, and SPINOL scaffolds through directed C−H bond activation.

Although various electrophiles have been employed for the directed *ortho*-C−H bond functionalization of phenols using noble metal such as Pd,[5] Rh,[6] Ru,[7] and Ir[8] catalysts, amidation using phenol derivatives has not been well explored.[9] Moreover, the amidation of the BINOL and SPINOL systems is largely not studied despite their potentiality as chiral ligands.[10] In 2013, Chang et al. reported a carbamate-directed sulfonamide synthesis using tosyl azide under iridium catalysis.[9a] Later, Singh et al. reported C−H amidation through intramolecular cyclization via an outer sphere pathway.[6f] Recently, Miura et al. demonstrated a copper-catalyzed amination reaction on phenols using bidentate auxiliary.[9b] To the best of our knowledge, phenol derivatives, that is, carbamate-directed C−H functionalization, have not been addressed under the cobalt catalysis. Driven by these facts and inspired by our continuous effort in cobalt catalyzed C−H functionalizations,[11] we set to develop carbamate-directed amidation and alkylation protocols under cost-effective, stable, high-valent cobalt(III) catalysis.[12−14]

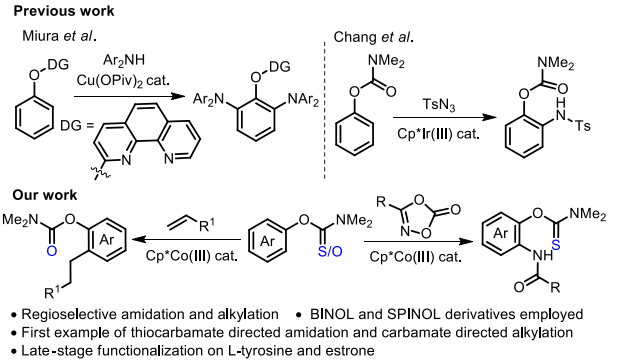
In line with the previous report by Ackermann et al.,[15] our attempts to conduct carbamate-directed amidation were also ineffective. We envisioned that tuning the polarizability of the coordinating atom by changing the directing group to thiocarbamate may solve the reactivity issue[16] and may also lead to specific reactivities toward a different set of electrophiles; however, the possibility of sulfur toxicity to transition metals is a serious concern.[17] This is probably the reason behind the lesser exploration of thiocarbamates as a directing group,[18] although versatile postsynthetic modifications are possible through Newman−Kwart,[19] anionic Fries,[20] and *O*-neophyl rearrangements of this directing groups.[21] Pleasingly,

Received: February 14, 2020

https://dx.doi.org/10.1021/acs.orglett.0c00589
Org. Lett. XXXX, XXX, XXX−XXX

switching the directing group from carbamate to thiocarbamate provided us the desired amidation products. On the contrary, in a similar catalytic system, thiocarbamate-directed alkylation was unfruitful; rather, it selectively reacted toward carbamates. Herein we report the first example of selective thiocarbamate- and carbamate-directed amidation and alkylation strategies under high-valent Cp*Co(III) catalysis (Scheme 1). These

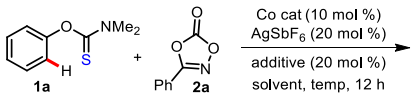
Scheme 1. Previous Reports and Our Work



methods responded well to various electronically different carbamates, amidating agents, and alkylating partners, thus opening an avenue for the direct access to valuable BINOL and SPINOL derivatives, which are reliable components for asymmetric catalysis.[1,10,22]

We initiated our optimization study using DCE as a solvent, Cp*Co(CO)I_2 (10 mol %) as a catalyst, $AgSbF_6$ (20 mol %) as an additive, 20 mol % of NaOAc as an acetate source, and phenyl dioxazolone **2a** as an amidating agent, and product **3aa** was isolated in 56% yield (Table 1, entry 1). After the screening of several solvents and acetate sources, the yield was improved to 62% (entries 2−6). Interestingly, whereas 60 mol % of KOAc retarded the reaction, 30 mol % of KOAc provided 65% of **3aa** (entries 7 and 8). The use of other cobalt catalysts

Table 1. Optimization of the Reaction Conditions[a,b]



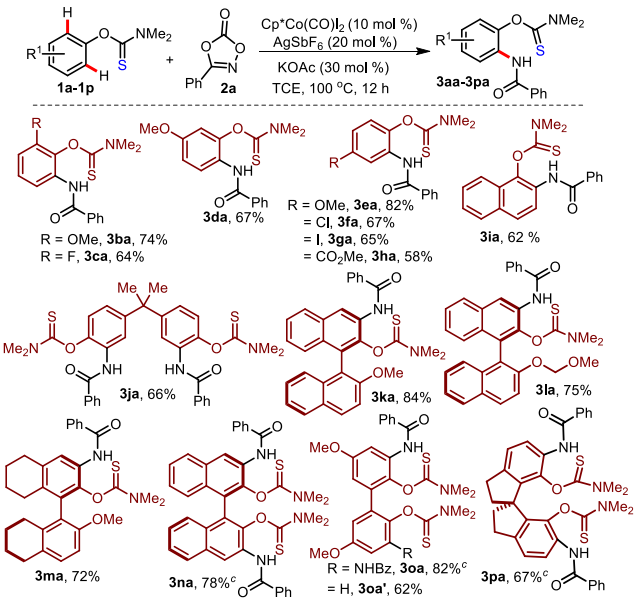
entry	solvent	catalyst	additive	temp (°C)	yield (%)
1	DCE	Cp*Co(CO)I_2	NaOAc	100	56
2	TFE	Cp*Co(CO)I_2	NaOAc	100	none
3	DCE	Cp*Co(CO)I_2	none	100	47
4	DCE	Cp*Co(CO)I_2	$Cu(OAc)_2$	100	none
5	DCE	Cp*Co(CO)I_2	KOAc	100	62
6	DCE	Cp*Co(CO)I_2	PivOH	100	59
7[c]	DCE	Cp*Co(CO)I_2	KOAc	100	none
8[d]	DCE	Cp*Co(CO)I_2	KOAc	100	65
9[d]	DCE	$CoCl_2$	KOAc	100	none
10[d]	DCE	$[Cp^*CoCl_2]_2$	KOAc	100	5
11[d]	**TCE**	**Cp*Co(CO)I_2**	**KOAc**	**100**	**73**
12[d]	TCE	Cp*Co(CO)I_2	KOAc	80	56
13[d,e]	TCE	Cp*Co(CO)I_2	KOAc	100	53

[a]Reaction conditions: thiocarbamate **1a** (0.2 mmol), oxazolone **2a** (0.4 mmol), catalyst (9.5 mg, 10 mol %), $AgSbF_6$ (13.7 mg, 20 mol %), additive (0.04 mmol, 20 mol %). [b]Isolated yield. [c]60 mol % of KOAc was used. [d]30 mol % of KOAc was used. [e]5.0 mol % of catalyst was used. DCE, 1,2-dichloroethane; TCE, 1,1,2,2-tetrachloroethane.

did not produce encouraging results (entries 9 and 10). Excitingly, switching of the solvent from DCE to TCE increased the yield up to 73% (entry 11). Further optimization of temperature and catalyst loading did not provide any better results (entries 12 and 13).

After optimizing the reaction conditions (Table 1, entry 11), first, the generality of the protocol was examined by employing a wide range of thiocarbamates **1** and amidating agent **2a** (Scheme 2). 2-Fluoro- and methoxy-substituted aryl thio-

Scheme 2. Scope of Aryl Thiocarbamates[a,b]



[a]Reaction conditions: thiocarbamates **1** (0.2 mmol), dioxazolone **2a** (0.4 mmol), TCE (1.5 mL). [b]Isolated yields. [c]20.0 mol % of Cp*Co(CO)I_2 and 40 mol % $AgSbF_6$ and 40 mol % KOAc were used.

carbamates successfully furnished the desired products **3ba−ca** in 64−74% yield. Methoxy substitution at the three-position delivered the product **3da** in 67% yield, indicating that the steric effect prevails over the electronic effect.[11e] The thiocarbamates bearing methoxy, chloro, and iodo substitutions at the para position were also suitable substrates (**3ea−ga**, 65−82% yield), providing an opportunity for further functionalization. Pleasingly, the electron-withdrawing ester group was also tolerated under the reaction conditions to provide **3ha** in 58% yield. The reactivity of α-naphthol has also been accessed to provide **3ia** in 62% yield. Doubly protected 2,2′-bisphenol was smoothly converted to diamidation product **3ja** in 66% yield. Considering the importance of asymmetric catalysis, different axially chiral common key building blocks for the ligand and catalyst were subjected to the reaction conditions. In this line, we switched our focus to sterically and electronically unique axially chiral BINOL derivatives. Thiocarbamate-protected (*R*)-BINOL **1k** readily reacted to offer amidation product **3ka** in an excellent yield of 84%. Gratifyingly, the MOM protecting group in **3la**, widely used in ligand synthesis, tolerated the reaction conditions. Likewise, the important octahydro-BINOL **1m** also underwent smooth amidation to afford **3ma** in 72% yield, keeping the four benzylic C−H bonds intact. Next, we switched our focus to unprecedented and challenging direct bis-C−H amidations of BINOL, biphenyl, and SPINOL in a regioselective manner,

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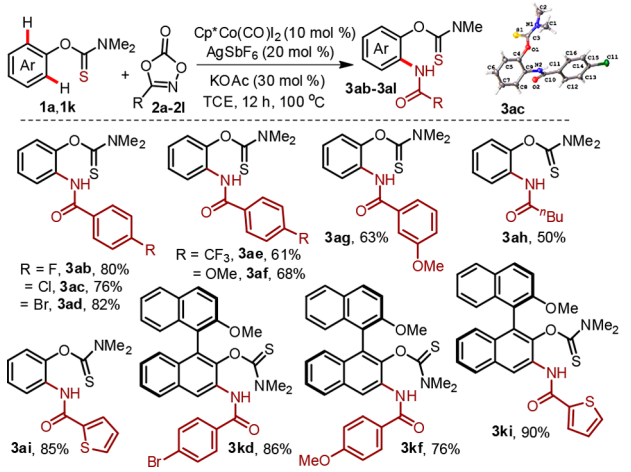
which can lead to a path for novel catalyst and ligand design.[1] The isolation of diamidation products **3na**−**oa** in 78−82% yield showed the efficiency and applicability of this method. It is important to note that the difunctionalization of BINOL and SPINOL by an ortho-lithiation strategy is often associated with the monofunctionalization side reaction. To our delight, the diamidation of SPINOL **3pa** was also achieved in 67% yield. It is noticed that BINOL thiocarbamates are more reactive toward amidation than simple phenol counterparts.

Next, the scope of amidating agent was investigated using thiocarbamate **1a** or **1k** as a coupling partner (Scheme 3).

Scheme 3. Scope of Dioxazolones[a,b]

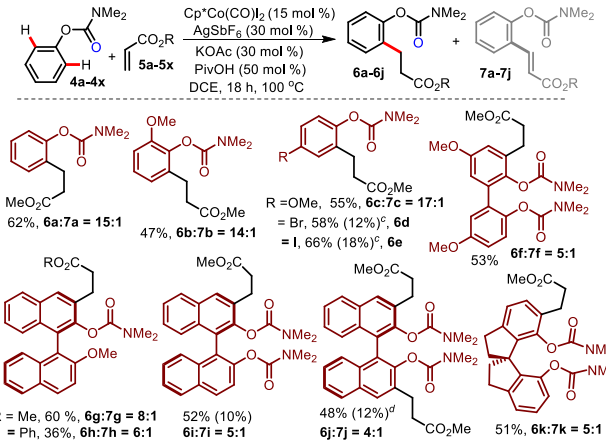


[a]Reaction conditions: Thiocarbamates **1** (0.2 mmol), dioxazolones **2** (0.4 mmol), TCE (1.5 mL). [b]Isolated yields.

Electron-withdrawing *para* fluoro-, chloro-, bromo-, and trifluoromethyl-substituted aryl dioxazolones reacted efficiently to provide **3ab**−**ae** in good to excellent yield (61−82%). Methoxy-substituted aryl dioxazolones also underwent smooth amidation (**3af**−**ag**, 63−68%). The reaction of butyl-dioxazolone was relatively sluggish and furnished **3ah** in 50% yield. Heteroaryl dioxazolone **2i** reacted efficiently to provide **3ai** in 85% yield. A series of BINOL derivatives **3kd**, **3kf**, and **3ki** were also synthesized in excellent yield (76−90%).

After establishing the amidation protocol, we switched our attention to develop an alkylation strategy under a similar catalytic system using thiocarbamate as a directing group; however, our attempts were in vain. Interestingly, upon replacing the solvent with DCE and changing the directing group to carbamate, the alkylated product **6a** was isolated in 40% yield, along with the formation of alkenylated side product **7a** in 10% yield (Scheme 4). To this point, the use of TCE did not provide any encouraging result for the alkylation reactions. Later, we found that the formation of **7a** was successfully suppressed upon the introduction of pivalic acid, and after the gradual increment, 50 mol % of pivalic acid furnished **6a** almost exclusively (62%, **6a**/**7a** 15:1). In the absence of KOAc, the use of 50 mol % pivalic acid solely offered **6a** but only in 38% yield. Carbamates bearing electron-donating methoxy substituents participated in the reaction to furnish **6b**,**c** in 47−55% yield. Pleasingly, bromo- and iodo-substituted carbamates were more reactive to afford **6d**,**e** in 58−66% yield along with the formation of 12−18% of dialkylation products. Biphenyl carbamate **4f** also responded well to produce **6f** in 53% yield. Considering the value of the

Scheme 4. Scope of Carbamate-Directed Alkylations[a,b]

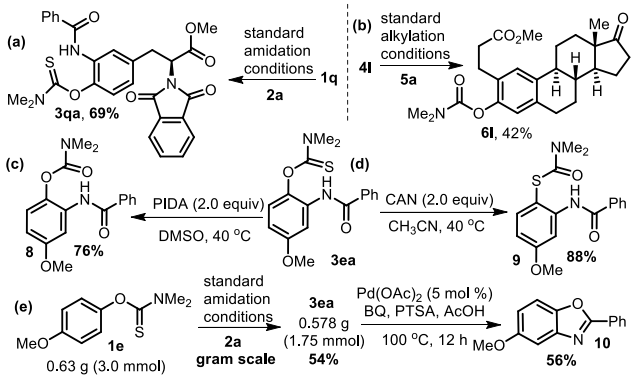


[a]Reaction conditions: carbamates **4** (0.2 mmol), arcrylates **5** (0.4 mmol), DCE (1.5 mL). [b]Isolated yields. [c]Dialkylation product has been reported. [d]30.0 mol % of Cp*Co(CO)I_2, 60 mol % $AgSbF_6$, and 40 mol % KOAc, 80 mol % PivOH were used.

products and the fact that the regioselective C3 alkylation of BINOL derivatives is a stiff task because the C6 position of the BINOL is more activated toward electrophilic substitution, we shifted our focus to direct the 3,3′-alkylation of BINOL dicarbamates. To our delight, BINOL derivatives **4g**−**i** responded well to accomplish alkylated products **6g**−**i** in 36−60% yield. The challenging dialkylated product **6j** was also synthesized in 48% yield by increasing the catalyst loading. The SPINOL dicarbamate was also viable to offer **6k** in 51% yield. Hence, this method can trigger a route for the modification of BINOL- and SPINOL-based chiral ligands.

The late-stage C−H bond functionalization is an efficient tool for rapid product diversification. Considering this fact, the tyrosine derivatives **1q** were subjected to the amidation conditions, and the desired product **3qa** was obtained in 69% yield (Scheme 5a). In another example, the late-stage

Scheme 5. Utilization of these Developed Methods



alkylation of estrone derivative **4l** provided **6l** in 42% yield (Scheme 5b). The versatility of the directing group was demonstrated by converting **3ea** to the carbamate **8** by using (diacetoxyiodo)benzene as an oxidant (Scheme 5c). Newman−Kwart rearrangement, a key reaction for sulfonic-acid-based catalyst design,[19] has been successfully performed on **3ea** to obtain compound **9** in 88% yield (Scheme 5d). A gram-scale synthesis was executed, and 0.58 g of amide **3ea** was isolated (Scheme 5e). To demonstrate the further utility of the

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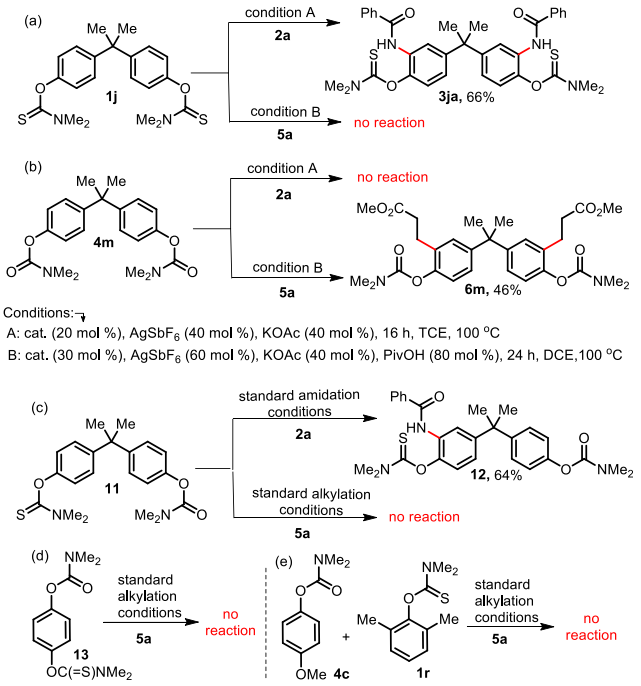
method, using the reaction conditions of Huang et al.,[18a] the biologically important heterocycle benzoxazole **10** has been synthesized from **3ea**.

To further validate the selective nature of the directing groups, **1j** and **4m** were subjected to amidation and alkylation conditions. Whereas dithiocarbamate **1j** responded promptly to the amidation conditions to furnish **3ja**, it was unreactive toward alkylation (Scheme 6a). On the contrary, although the

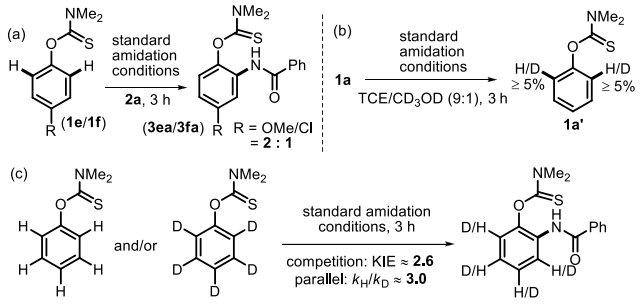
Scheme 6. Proof of Selective Reactivity of the Directing Groups



dicarbamate **4m** did not provide any amidation product, it reacted smoothly to provide alkylated product **6m** in 46% yield (Scheme 6b). This directly demonstrates the specific reactivity of the carbamate and thiocarbamate directing groups. Later, substrate **11** bearing both carbamate and thiocarbamate directing groups was exposed to the amidation conditions, which produced the amidation product **12**, but interestingly, no alkylation product was obtained under standard alkylation conditions (Scheme 6c). These results suggest that in a competition, thiocarbamate wins over the weakly coordinating carbamate to form the cyclometalated species, which provide only the amidation product, not the alkylated one. This conclusion was supported by the unsuccessful alkylation of compound **13** (Scheme 6d). These reactivity patterns may have originated from the coordinating ability of electrophiles to the cyclometalated species **B** and **E** (Scheme 8). We believe that thiocarbamate **1a** and electrophiles compete for coordination to **B**, where strongly coordinated **2a** might win over **1a**, which may not be the case for **5a**. Sulfur toxicity toward the alkylation reaction was further corroborated by the ineffective alkylation reaction in the presence of compound **1r** (Scheme 6e).

The preferential conversion of **1e** over **1f** in a 2:1 ratio (**3ea**/**3fa**) suggests that the reaction proceeds through a base-assisted internal electrophilic substitution (BIES) reaction-type mechanism (Scheme 7a).[23] The lack of significant H/D scrambling at the ortho positions of **1a**, in the presence of d_4-

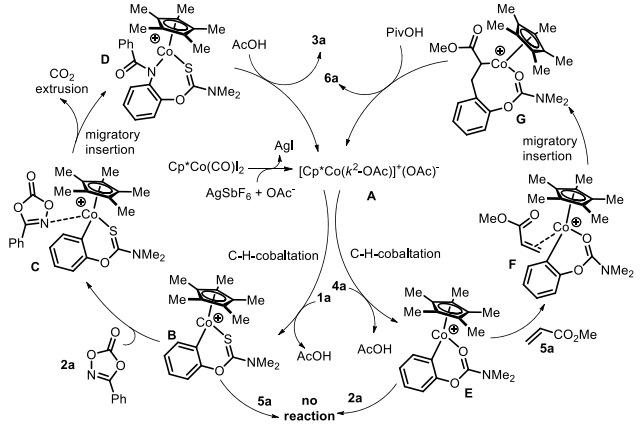
Scheme 7. Mechanistic Studies



acetic acid, suggests that an irreversible C−H activation step is involved here (Scheme 7b). Finally, the kinetic isotopic effect (KIE) value of 2.6 from the intermolecular competition experiment and the K_H/K_D value of 3.0 from a parallel experiment between **1a** and [D_5]-**1a** indicate the rate-determining C−H activation step (Scheme 7c).

Relying on our mechanistic studies and previous reports,[24] a plausible catalytic cycle is proposed, where in the presence of $AgSbF_6$ and KOAc additives, catalyst Cp*Co(Co)I_2 is assumed to transform into active species **A** (Scheme 8). Cp*Co(III)

Scheme 8. Proposed Mechanism



complex **A** generates a kinetically relevant metallacycle **B** through the acetate-assisted C−H activation. After coordination through the nitrogen center of dioxazolone **2a**, species **C** is formed, which undergoes migratory insertion through CO_2 extrusion to form amido-inserted species **D**. After that, protodemetalation occurs in the presence of AcOH to offer amidation product **3aa**, and the active catalyst **A** is regenerated, thus completing the catalytic cycle. In another catalytic cycle, cobaltacycle **E** undergoes coordination to acrylate **5a** to form species **F**. Then, the migratory insertion followed by protodemetalation in the presence of pivalic acid provides **6a** along with the active catalyst **A**.

In conclusion, we developed directing-group-specific C−H bond amidation and alkylation strategies for phenol derivatives under cost-effective, stable, high-valent cobalt(III) catalysis. The successful responses from various carbamates, dioxazolones, and arylates exhibit the versatility of this method. Amidation and alkylation on BINOL and SPINOL derivatives disclose a significant route for the further development of these chiral ligands. The supremacy of this method was further revealed through the late-stage C−H functionalization of L-

https://dx.doi.org/10.1021/acs.orglett.0c00589
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tyrosine and estrone derivatives. We believe that this method can be instrumental for designing new chiral ligands.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00589.

Experimental procedures, spectroscopic data, and NMR spectra of compounds (PDF)

Accession Codes

CCDC 1978184 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.S.M. gratefully acknowledges SERB, Department of Science and Technology, New Delhi, India (sanction no. CRG/2018/000317) for funding. S.S.B. acknowledges CSIR, India for the fellowship.

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https://dx.doi.org/10.1021/acs.orglett.0c00589
Org. Lett. XXXX, XXX, XXX−XXX